ON TETROLIC ACID

INAUGURAL-DISSERTATION

DER

MATHEMATISCHEN UND NATURWISSENSCHAFTLICHEN FAKULTÄT

DER

KAISER-WILHELMS-UNIVERSITÄT STRASSBURG

ZUR ERLANGUNG DER DOCTORWÜRDE

VORGELEGT VON

M. C. CLUTTERBUCK

London (England).

STRASSBURG

Printed by J. H. Ed. Heitz (Heitz & Mündel)

1891.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41542727_0039

ON TETROLIC ACID.

INTRODUCTION.

The following experiments on tetrolic acid were untertaken at the suggestion of Professor Fittig, and I take this opportunity of thanking him for the help which he has given me in the course of the investigations.

Most of the experiments had been already performed, but as the results obtained by different chemists were more or less conflicting, Professor Fittig thought it desirable to repeat their work; more especially with regard to the action of sodium amalgam, bromine, and hydrobromic acid upon tetrolic acid.

For some time, almost the only known acid belonging to the series $C_nH_{2n}{}_{-4}O_2$ was sorbic acid, first prepared by Hofmann[1] from the juice of the unripe berries of the mountain ash.

But this acid, as shewn by Professor Fittig[2] probably does not contain the group —C≡C— but possesses the formula

$$CH^3 - CH = CH - CH = CH - CO - OH$$

Subsequently Palmetolic stearolic and Behenolic acids were discovered, belonging to this series, and Baeyer and his school showed that by the indirect removal of hydrogen from the higher members of the acids of the oleic series, they could be converted into the corresponding members of this series. The constitution of many of these however is still a matter of un-

---

1 Ann. 110, 129.

2 Ann. 161, 307.

certainty. Tetrolic acid itself was first discovered by Geuther,[1] who obtained it by treating the ester of β monochlorocrotonic acid (melting pt. 94.5°) with a solution of caustic potash.

„For the preparation of this acid it is convenient to use the oily body produced by the action of phosphorus pentachloride upon aceto acetic ether, which consists of a mixture of the esters of β chlorocrotonic (m. p. 94) and β chlorisocrotonic (m. p. 59. 5) acid. The oil is mixed with rather more caustic potash solution than is required to completely decompose the ester, a certain amount of alcohol is added and the whole warmed on a water bath in a flask connected with an inverted condenser, until the oily body has completely disappeared.

If the liquid becomes neutral before this occurs some more caustic potash solution is introduced, but a large excess of the latter is to be avoided, as the tetrolic acid itself is thereby decomposed.

The contents of the flask are then distilled until no more alcohol passes over, acidified with sulphuric acid and again distilled till the unaltered β chlorisocrotonic acid has been entirely removed.

The acid residue is then extracted with ether, free from alcohol, the ethereal solution dried by means of calcium chloride, and the ether distilled off on a water bath.

The mass of brown colored crystals which remain on cooling can be rendered colorless by repeated recrystallisation from water and consist of the pure acid.

The tetrolic acid thus prepared crystallises in colorless transparent rhombic tablets, very soluble in water and deliquescent in moist air. The melting, point of the acid dried over sulphuric and is 76. 5 solidifying pt. 76. 5. Geuther also attempted to prepare the acid directly from monochlorocrotonic acid, or as he calls it monochlorotetracrylic acid (m. p. 94). To 2 grams of the latter acid were added three times the amount of caustic potash dissolved in water that was required for neutralising the acid. The mixture was heated for twelve hours on a water bath, the evaporated water being replaced from time to time.

[1] Zeitsch. für Chem. 1871, 265.

The liquid was acidified with sulphuric acid and extracted with pure ether. All the chlorocrotonic acid was decomposed, but only a very small amount of tetrolic acid was formed, the greater part of the acid being converted by the action of the caustic potash into acetone and carbon dioxide. According to Geuther the β chlorisocrotonic acid, or as he calls it monochloroquartenylic acid is not decomposed by boiling with a solution of caustic potash. Lagermark[1] succeeded in synthesising tetrolic acid by the action of carbon dioxide upon sodium allylene $C_3H_3N_a$ thereby proving that it possesses the formula CH_3 C≡C—COOH. Asymmetrical, allylene CH_3C : CH prepared from bromopropylene was passed into well cooled ether whereby a considerable quantity of the gas was absorbed. Sodium acted upon the solution with evolution of hydrogen and formation of sodium allylene, which was insoluble in ether and was precipitated in the form of a white crystalline powder. Carbon dioxide acts very energetically upon this substance, so much so that even when the flask is well cooled, carbonisation takes place, unless the addition of the carbon dioxide is made very gradually. On this account a stream of carbon dioxide was led very stowly over the powder and the sodium salt $C_4H_3O_2N_a$ was produced. The free acid is identical with the acid prepared by Geuther from monochlorocrotonic acid, crystallises in colorless transparent tablets, is readily soluble in water alcohol and ether, does not deliquesce in the air, but does so readily under a belljar whose sides are moistened with water, melts at 76° and distils apparently with partial decomposition at 197—205. The acid is odorless, difficultly volatile with steam and takes up bromine. The addition product is at first liquid, but changes with the evolution of hydrobromic acid to a solid crystalline mass. Pinner[2] succeeded in producing tetrolic acid by the action of sodium and carbon dioxide upon allylene chloride.

„To a mixture of equal parts of allylene chloride and benzine thin strips of sodium were gradually added and a stream of carbon dioxide passed through the mixture. The sodium changed

---

[1] Ber. XII, 854

[2] Ber. 1881, 1081.

pretty rapidly to a brown mass, which after passing carbon dioxide for a long time became lighter coloured. In order to completely convert 75 grams of allylene chloride to which 32 grams of sodium had been added it is necessary to pass carbon dioxide for about 8 days. When the reaction was complete, the benzene was poured off from the solid mass, which was washed with ether and dissolved in water under ether in order to remove the last traces of petroleum which had adhered to the sodium. The clear watery solution, after acidifying with dilute sulphuric acid was extracted with ether. The ethereal solution was freed from ether by evaporation and the residue sublimed from an oil bath at 150°. Long colorless shining needles which melted at 76° were thus obtained. Analysis proved the acid, whose properties have been sufficiently described by Geuther, to possess the formula $C_4H_4O_2$.

Friederich[1] succeeded in obtaining a better yield of tetrolic acid from monochlorocrotonic acid than Geuther had done, and also in obtaining a good yield from monochloris ocrotonic acid (m. p. 59. 5) which according to Geuther is not decomposed by boiling with caustic potash.

To obtain tetrolic acid from the latter, an aqueous solution of caustic potash was used in which every 100 cbcm contained 7. 46—7. 99 grams of KOH, and to every two grams of potassium chlorisocrotonate 3.57 grams (2 mol) of KOH were added the mixture being healed in an oil bath for 20 or 30 minutes from 125°—135°. In this case the destillate was not odoress and yielded, on addition of sodium carbonate, an oily layer of acetone, recognised by its combining with sodium bisulphite, but the amount obtained from 40 grams was so small that its boiling point could not be determined. The residue, after acidifying with sulphuric acid and extracting with ether, yielded a substance, at first syrupy, but after standing for some time over sulphuric acid, becoming completely crystalline. The yield was good, 45 grams of the not quite dry potassiumsalt of chlorisocrotonic acid yielded between 19 and 20 grams of acid free of chlorine. The body after recrystallising from carbon disulphide gave a con-

[1] Ann. 219, 342.

stant melting pt of 76—76.5 and its analysis proved it to be tetrolic acid.

In order to convert β chlorocrotonic acid (m. p. 94) into tetrolic acid Friederich used a solution of caustic potash in which every 100 cbcm contained about 6.6 grams of KOH. From five grams of potassium salt (1 mol) which had been healed on an oil bath for 2 hours from 70° to 80° with 2 grams of KOH (1.77 grams = 1 mol) in a solution of the above strength, after acidifying and shaking out twice with ether 2.3 grams were obtained, the theoretical amount being 2.65. Tetrolic acid prepared in this way possessed the characteristics described by Geuther Lagermark etc.

Moreover Friederich obtained additional proof that the tetrolic acids from whatever source obtained were identical and possessed the formula CH_3 C : C COO H, by oxidising specimens of tetrolic acid obtained from β chlorocrotonic acid (m. p. 94°) and also from β chlorisocrotonic acid (m. p. 59.5) according to the hitherto accepted formula for β chlorisocrotonic acid, tetrolic acid prepared from this source might have either of the two formulae given in the following equations

$$\begin{array}{l} CH_2 \\ \| \\ CCl \\ | \\ CH_2 \\ | \\ COOK \end{array} + KOH = \begin{array}{l} CH_2 \\ \| \\ C \\ \| \\ CH \\ | \\ COOK \end{array} + KCl + H_2O$$

or

$$\begin{array}{l} CH_2 \\ \| \\ CCl \\ | \\ CH_2 \\ | \\ COOK \end{array} + KOH = \begin{array}{l} CH \\ \| \\ C \\ | \\ CH_2 \\ | \\ COOK \end{array} + KCl + H_2O$$

while the tetrolic acid formed from the chlorocrotonic acid which melts at 94° could only possess one of the following formulae.

$$\begin{array}{l} CH_2 \\ \| \\ C \\ \| \\ CH \\ | \\ COOH \end{array} \quad \text{or} \quad \begin{array}{l} CH_2 \\ | \\ C \\ \| \\ C \\ | \\ COOH \end{array}$$

The first of these two is however inadmissible after the researches of Lagermark and therefore if the hitherto generally accepted formula for the two β chlorocrotonic acids were correct, the tetrolic acid formed from the one would be isomeric and not identical with that formed from the other. Both however on oxidation with permanganate of potash yield acetic acid, which is only possible on the assumption that both possess the group CH_3—C and are in fact represented by the formula indicated by the synthesis made by Lagermark, namely CH_3 C:C COOH· Such, briefly, is the state of our knowledge of tetrolic acid at present.

For the following experiments tetrolic acid was prepared with but slight modification of the method given by Friederich. [1] The product of the action of phosphorus pentachloride upon aceto acetic ether was first heated to 115° in order to distill off as much as possible of the phosphorus oxychloride formed in the reaction, then dissolved in water and distilled with steam. The difficultly volatile chlorocrotonic acid was extracted directly from the residual liquid with ether and the raw acid so obtained was decomposed with an aqueous solution of caustic potash of the strength recommended by Friederich. The distillate consisting of a mixture of the volatile acid and the neutral oil was neutralised and the oil was distilled off and treated with alcoholic potash as recommended by Kahlbaum. The residue was then acidified with sulphuric acid and the readily volatile chlorisocrotonic acid was distilled over, this was decomposed with aqueous potash hydrate solution as recommended by Friederich.

The tetrolic acid obtained from these sources was recrystallised from ligroin. Friederich recommends recrystallising from carbon disulphide but I was able to obtain pure crystals more readily from ligroin. The acid so obtained melted at 76°-77° and proved on testing to be free from chlorine.

---

[1] Ann. 219, 343.

ACTION OF SODIUM AMALGAM UPON TETROLIC ACID.

According to Aronstein and Holleman[1] tetrolic acid is converted in aqueous solution by sodium amalgam into solid crotonic acid. The above mentioned chemists treated five grams of tetrolic acid with an excess of 3 percent sodium amalgam, left to stand for 24 hours acidified, distilled with steam, neutralised the distillate, evaporated, reacidified and extracted the acid with ether which was free from alcohol, they thus obtained crystals which on recrystallising from hot water gave a melting pt. of 72° which is the melting point of solid crotonic acid (that of tetrolic acid being 76°). The zinc salt was also prepared and it was hence inferred that this substance was crotonic acid, though an analysis is not given. It was moreover assumed that tetrolic acid is not volatile with steam and therefore that the distillate must contain crotonic acid. „Da die Tetrolsäure mit den Wasserdämpfen nicht flüchtig ist, musste die überdestillirende saure Flüssigkeit die gebildete Crotonsäure enthalten."

I have found on the contrary that tetrolic acid is volatile with steam, although it passes over slowly and a large amount of water must be distilled over, before much of the acid is obtained.

Five grams of tetrolic acid were dissolved in water and ten times the theoretical amount of sodium amalgam (containing 4 per cent of sodium) required for the addition of 2 atoms of hydrogen was gradually added, the liquid was kept as nearly neutral as possible by the addition from time to time of sulphuric acid. Since however five days were required before all the sodium amalgam was used up and since on standing over night the liquid was always found to be strongly alkaline in the morning the experiment is equivalent to two, one in a neutral, the other in an alkaline solution.

When all the sodium amalgam had been used up the solution was acidified with sulphuric acid, filtered off from the mercury and extracted with ether which was free from alcohol. After

---

[1] Ber. XXII, 1181.

distilling off most of the ether the residue was placed in a beaker glass and began at once to deposit crystals. It was left over night in vacuo over sulphuric acid and then recrystallised from ligroin. 4.85 grams of tetrolic acid melting at 76.5 were thus obtained.

Five grams of tetrolic acid were then dissolved in water and healed to 100° in a water bath and 10 times, the amount of sodium amalgam required for the addition of 2 atoms of hydrogen was gradually added, the liquid being neutralised from time to time with sulphuric acid.

The solution was diluted acidified with sulphuric acid and distilled with steam. On neutralising the distillate with barium carbonate and evaporating, the amount of salt obtained was too small to permit of its investigation. It was inferred that sufficient care had not been given to keep the liquid neutral and that the tetrolic acid had been destroyed by boiling with excess of alkali.

Accordingly another experiment was performed, 5 grams of tetrolic acid were treated with 10 times the theoretical amount of sodium amalgam required for the addition of two molecules of hydrogen, at the temperature of 100° on a water bath, care being taken to keep the liquid neutral by frequently testing and adding dilute sulphuric acid, from time to time as required. The solution was diluted, acidified with sulphuric acid, and distilled with steam for several days, until the distillate no longer gave an acid reaction with litmus paper, the distillate was neutralised with barium carbonate and evaporated, the barium salt was decomposed with dilute hydrochloric acid and extracted with pure ether.

The melting point of the acid, recrystallised from ligroin was 76.5 an analysis of the acid gave the following numbers

amount of acid taken	·2225
water found	·1011
carbon dioxide	·4650

calculated for crotonic acid	percentage found	calculated for tetrolic acid
6·97	H 5.04	4·76
55·80	C 56·98	57·14

According therefore to the above experiments it would seem that crotonic acid is not produced by the action of sodium amalgam upon tetrolic acid, and these results are confirmed by a subsequent experiment, in which dibromocrotonic acid on treating with sodium amalgam yielded tetrolic and not crotonic acid. In this latter experiment it may be fairly assumed that as the bromine atoms were removed the liberated carbon affinities would have a greater tendency to unite each with an atom of hydrogen than when these two affinities are already combined with each other as in the case of tetrolic acid.

The action of hydrobromic acid upon tetrolic acid was next investigated.

According to Michael and Browne[1] three different monobromocrotonic acids have been prepared.

1) The acid derived from α dibrombutyric acid CH_3 CH_2 CBr_2 COOH. This can only have the formula of α bromocrotonic acid CH_3 CH : CBr COOH. Its melting point is 106.5.

2) β or as they prefer to call it αllo α bromocrotonic acid, the acid obtained by Kolbe[2] by acting on αβ dibromobutyric acid (the product of the addition of bromine to solid crotonic acid) with an aqueous solution of caustic potash. This acid melts according to Kolbe at 90°, according to Michael and Norten at 92° and crystallises from ligroin in needles that are readily powdered. Its barium salt crystallises with $3^1/_2$ molecules of water.

3) An acid obtained by the action of hydrobromic acid upon tetrolic acid, melting after repealed crystallisation from ligroin at 94.5 and crystallising from that liquid in very characteristic feathery plates which can only be powdered with difficulty and yielding a barium salt which crystallises with one molecule of water.

---

1 Jour. pract. chem. 35, 258. Am. chem. jour. IX, 279.

2 Jour. pract. chem. 25, 394.

Since the difference of melting point of the two last mentioned acids is small and since it is difficult to give formulae representing these three isomeric acids, unless we admit some such hypothesis as that of van't Hoff it was thought advisable to repeat these experiments. Two grams of tetrolic acid were dissolved in a large excess of fuming hydrobromic acid solution saturated at 0°. The next morning the mass was almost solid, the crystals were drained on a platinum cone and washed with a small amount of water, which precipitated a fresh quantity of acid from the mother liquor. The crystals, after pressing and drying over sulphuric acid and caustic potash in vacuo, were recrystallised several times from ligroin till they showed a constant melting point of 93.5. An analysis of the acid gave the following numbers

Substance taken	.2330
weight of Ag Br found	.2668

	found	calculated for monobromoroton acid
percentage of bromine	48·72	48·48

α. β dibromobutyric acid was then prepared by adding bromine dissolved in carbondisulphide to a solution of solid crotonic acid in carbon disulphid. The dibromobutyric acid so obtained was treated with a moderately concentrated solution of sodium hydrate, the whole being healed for a short time on the water bath till the raction was complete. The solution was then acidified with dilute sulphuric acid and the whole rapidly changed to a semisolid mass, the precipitated acid was washed on a platinum cone with a small amount of water, dried and recrystallised from ligroin till the melting point remained constant at 91°. The difference of melting point between the two acids is perhaps not alone sufficient to prove clearly their difference, but their appearance and physical properties are also very different as Michael observes, the acid derived from tetrolic and hydrobromic acids crystallisses from ligroin in feathery leaflets which are very difficult to pulverise, while that obtained from α β dibromobutyric acid crystallises in fine needles that are easily pulverised I have crystallised both acids several times from ligroin and found these characteristics always to hold good.

The barium salts of the acids were prepared by boiling them in aqueous solution with barium carbonate; the salts showed a marked difference of crystalline form, that of the acid melting at 91° crystallised in prismatic needles, containing $3^1/_2$ molecules of water; that of the acid melting at $93^1/_2$, in fine laminae containing 2 molecules of water. An analysis of the barium salt of the acid melting at 91° gave

weight of air dried salt taken	·2321
loss of wt of water at 100°	·0281
water of crystallesation found	12·10 percent
calculated for $3\,^1/_2$ H_2O	11·93
wt of anhydrous salt	·2040
wt of barium sulphate	1029
percentage of ba found	29·65
percentage calculated	29·46

The barium salt of the acid obtained from tetrolic acid gave on analysis 2 molecules of water of crystallisation thus

weight of air dried salt	·2071
loss of water at 100°	·0158
percentage of H_2O found	7·63
calculated for 2 H_2O	7·10

It is clear therefore that the two acids are not identical and the question remains as to what formulae are to be assigned to the three known bromocrotonic acids.

As Michael observes,[1] the constitution of two of the three known bromocrotonic acids is hardly open to doubt. If, as seems reasonably certain, α dibromobutyric acid has the constitution usually assigned to it, their α bromocrotonic acid, (m. p. 106) obtained from it by the elimination of hydrobromic acid can have no other constitution than CH_3 CH : C Br COOH. In regard to the new acid formed by the addition of hydrobromic acid to tetrolic acid, it is safe to assume relying on the rule that the halogen takes the β position with regard to the carboxyl group and that chlorydric acid unites with tetrolic acid to form β chlorocrotonic acid, that we have in this acid a β bromocrotonic

[1] Am. chem. jour. IX, 287.

acid of the constitution CH_3 CBr : CH COOH. The formation of the 3rd bromocrotonic acid from α β dibromobutyric acid admits of three different interpretations

$$CH_3\,CHBr\,CHBr\,COOH = \begin{cases} (1)\ CH_3\,CH : CBr\,COOH + HBr \\ (2)\ CH_3\,CBr : CH\,COOH + HBr \\ (3)\ CH_2 : CH\,CHBr\,COOH + HBr \end{cases}$$

Michael then goes on to observe that unless we assume the possibility of two chemical isomerides being represented by the same structural formula, the formulae marked (1) and (2) are impossible, as acids of these formulae have been obtained and are found to be different from the acid in question. He then proceeds to give various reasons for rejecting the 3rd formula mentioning in particular the remarkable differences noticed in the decomposition of α β dibromobutyric acid and its ethyl ether as showing the improbability of the third acid having the formula CH_2 CH CHBr COOH. He would therefore assign to this acid the formula usually given to α monobromocrotonic acid and to distinguish it from the latter compound names it allo α bromocrotonic acid.

But, as he observes, if this formula be correct, it is necessary to change the law on the decomposition of α β halogen acids stated by Erlenmeyer,[1] that in removing hydrobromic acid α halogen and β hydrogen are principally eleminated. It is also necessary to adopt some such theory of allo isomerism as that suggested by Wislicenus (Ueber die räumliche Anordnung der Atome in organischen Molekülen) which he adopted principally from an investigation of the isomerism of fumaric and maleic acid.

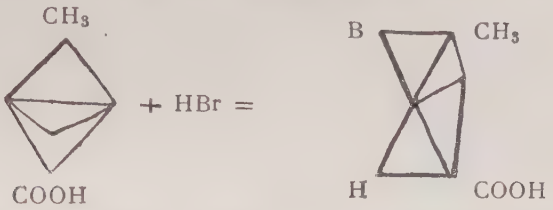
If however we adopt the latter hypothesis it is possible to assign formulae to all three acids without changing Erlenmeyers law. For the first acid melting at 106° we retain the formula α bromocrotonic acid thus CH_3 CH CBr COOH.

The acid obtained by the addition of hydrobromic and to

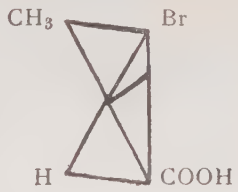
---

[1] Ber. 15, 49.

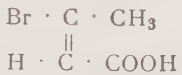
tetrolic acid (93.5°) would be β bromocrotonic acid and its formation would be graphicaly represented, according to Wislicenus'



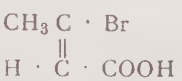
theory thus while the third acid obtained from α β dibromobutyric acid by the action of caustic potash would also be β bromocrotonic acid and would be represented by the reflexion of the formula given for the other β bromocrotonic acid thus or adopting the shortened formulae given by Wislicenus the one acid will be



represented thus : —



The other thus : —



The action of bromine on tetrolic acid was next investigated.

Lagermark[1] observes that on the addition of bromine to tetrolic acid, a liquid is first formed which soon becomes solid with disengagement of hydrobromic acid.

Pinner[2] says that tetrolic acid unites readily with two atoms of bromine to form a compound, at first liquid, but soon becoming solid and that no disengagement of hydrobromic acid could be observed.

The substance so obtained melted at from 95°—97° and ryielded on analysis 66.3% of bromine, the calculated percentag foedibromocrotonic acid being 65.57.

---

[1] Ber. XII, 885.

[2] Ber. 1881, 1081

Pinner further observes that in the cold, tetrolic acid does not combine with more than two atoms of bromine.

Michael and Pendleton[1] prepared tribromobutyric acid by addition of bromine to monobromocrotonic acid, and on treating the acid so obtained with alcoholic potash an α β dibromocrotonic acid was obtained melting at 94°. According to these chemists, this acid is identical with the dibromocrotonic acid prepared by Pinner. The crystalline form is described by them as that of an oblique truncated prism, and the barium salt crystallises with $3^1/_2$ molecules of water.

The results obtained in the following experiments are completely, at variance with those just described.

To 2 grams of tetrolic acid suspended in carbondisulphide. the calculated amount of bromine required for the addition of 2 atoms of bromine to the molecule, dissolved in carbon disulphide was gradually added, drop by drop from a separating funnel whose end had been drawn out to a capillary tube. (The cylinder in which the mixture took place was kept at 0° being surrounded by ice water. After standing for some time the colour did not completely disappear and a yellow flocculent precipitate was formed. On removing the stopper quantities of hydobronic acid were evolved, the stopper was immediately replaced and the carbon disulphide evaporated at the ordinary temperature of the laboratory by passing a current of dry air through the solution. There remained a small quantity of dark colored matter which after placing in vacuo over caustic potash solution all night was found next morning to still emit fumes of hydrobromic acid when exposed to the air, no crystals could be obtained there from.

The experiment was repeated several times with the same results.

It is possible that the reason for this want of success is to be found in the fact that tetrolic acid is practically insoluble in ice cold carbon disulphide, and instead of a solution of the acid, the solid particles of the acid were exposed to the action of the bromine.

---

[1] Jour. pract. chem. 38, 2.

Two grams of tetrolic acid were then dissolved in chloroform previously rendered free from alcohol by repeatedy agitating with water and finally dried by means of calcium chloride.

The whole was then placed in a vessel containing ice water, and the calculated amount of bromine required for the addition of two atoms of bromine was dissolved in pure chloroform and slowly added to the mixture by means of a separating funnel drawn out to a fine point. The solution was run in very slowly about $2^{1}_{,2}$ hours being required to complete the addition and the liquid was repeatedly agitated. Decoloration took place at first slowly, afterwards more rapidly and the liquid at last was completely colourless. On opening the stopper, in one instance no hydrobromic acid was observed, in another a very small quantity only. The chloroform was evaporated in a current of dry air at the ordinary temperature and the compound was obtained in the form of a white powder, the yield being almost theoretical. The compound was dissolved in chloroform slightly warmed and left to stand, next morning small well defined crystals, somewhat resembling calc spar were found deposited at the bottom of the beaker glass which after drying carefully gave a melting point o 115°. Repeated recrystallisation from chloroform gave crystals of a constant melting pt 119.8—120.4 A small quantity of very pungent oil attacking the eyes and nose was also formed, but the amount was too small to permit of its investigation. A bromine determination of the compound gave the following numbers.

Substance taken	.20405
wt of Ag Br formed	·3144
percentage of	% of bromine

bromine found	calculated for debromocrotonicacid
65·42	65·57

A second bromine determination gave the following numbers

substance taken	·2399
wt of Ag Br	·3706

	found	calculated
%	65·73	65·57

A combustion of the substansce was next made and gave the following numbers

Substance taken	·2160
wt of H_2O produced	·0410
wt of CO_2 produced	·1564

	found	calculated
percentage of H	2·10	1·64
percentage of C	19·74	19·66

A second combustion gave

substance taken	.2452
wt of H_2O produced	·0383
wt of CO_2 produced	·1769

	found	calculated
percentage of H	1·73	1·64
percentage of C	19·68	19·66

There can therefore be no doubt that this body is dibromocrotonic acid CH_3 CBr : COOH, through its melting pt. 120° differs so widely from that of the body obtained by Pinner whose melting point he gives at 95°—97°. It certainly seems impossible that two isomeric bodies could be formed by the addition of 2 atoms of bromine to a molecule of tetrolic acid. Pinner does not give details as to the manner in which the bromination of the tetrolic acid was performed.

The crystals obtained by slowly evaporating a chloroform solution of the new acid are well defined and were measured by Mr. Burwell in the mineralogical institute under the superintendance of Dr. Link. The following results were obtained by him.

System monosymmetric

$$a : b : c = 1{,}1907 : 1 : 1{,}6692$$
$$\beta = 80°55.5'$$

observed forms : —

$C - O\ P\ [001]$, $m = \infty P\ [110]$, $r = P \infty\ [10\bar{1}]$.

(Figure)[1].

---

[1] See «Zeitschrift für Krystallographie» XIX, 5.

The following angles were measured and calculated

	measured	calculated
$(1\bar{1}0) : (110)$	= *98°41′	—
$(001) : (\bar{1}10)$	= *84°8′	—
$(00\bar{1}) : (10\bar{1})$	= *68°10.5	—
$(101) : (10\bar{1})$	= 55°20′	56°0′

The faces did not for the most part give well defined images, hence it was impossible to carry out the measure ments with the accuracy that could be desired.

The crystals generally presented the appearance of rhombohedra, on many of them the face P ∞ is wanting, but on all of them the base and the prism are well developed. There is a very perfect cleavage parallel to the base and a good cleavage parallel to the primary hemidome r = P ∞.

The plane of the optic axes is perpendicular to the plane of symmetry and to the primary hemidome. The angle of the optic axes was measured in a section parallel to r and with sodium light, the following value was obtained. 2 Ea = 56°1′.

The new acid was found to be readily soluble in alcohol ether and hot chloroform, less so in cold chloroform and still less so in ligroin on addition of the latter to a cold concentrated chloroform solution the acid is precipitated in fine needles which on standing for a few days become converted into small tablets.

The acid was also found to be moderately soluble in hot water, whence it crystallises on cooling in the form of beautiful white needles, and being very insoluble in cold water, this forms a very convenient method of purifying the acid.

After boiling a portion of the acid for a short time with water the solution was tested with silver nitrate for hydrobromic acid, and it was found that no decomposition had taken place. The acid volatilises slowly at 100° without decomposition.

A silver salt of the acid was next prepared by neutralising an aqueous solution of the acid with ammonia and adding a solution of silver nitrate, a white precipitale of the silver salt was at once throm dowm. This after washing to free from

ammonium and silver nitrates, was redissolved in hot water, in which it is readily soluble, on cooling the solution the salt crys. tallesed out in the form of very fine transparent leoflets which do not seem to be particularly sensitive to light.

An analysis of the silver salt gave

amount of salt taken	·1779
Ag Br obtained	·0945

	found	calculated
percentage of Ag	30·52	30·70

The barium salt of the acid was also prepared by boiling an aqueous solution of the acid with barium carbonat. It is very soluble in hot water, less so in cold water and crystallises from a warm solution in small prisms containing 3 molecules of water.

An analysis gave the following results.

amount of air driedsalt	·2453
loss of H_2O on heating to 100°	·0198

	found	calculated for 3 mol H_2O
H_2O =	8·07	7·99

Amount of an hydrous salt	·2255
Ba SO_4 formed	·0845

	found	calculated
percentage of Ba	22·03	21·99

Action of sodium amalgam on dibromocrotonic acid.

Three grams of the acid were treated with ten times the theoretical amount 4 % sodium amalgam required for the substitution of hydrogen for the bromine. The addition was made gradually the solution being kept neutral or only slightly alkaline by the addition of dilute sulphuric acid from time to time. The solution was then acidified with sulphuric acid and extracted with ether. The ether was distilled off and the residue crystallised in vacuo over sulphuric acid. The acid after recrystallising from hot ligroin melted at 76° — 77° which is the melting point of tetrolic acid. An analysis proved that it was in reality this acid thus

Substance taken	·2440
H_2O produced	·1083
CO_2 produced	·5113

	found	calculated
percentage of H	4·92	4·76
percentage of C	57·14	57·14

It would seem therefore that the action of sodium amalgam upon dibromocrotonic acid consists merely in removing the bromine and not replacing it by hydrogen. This experiment also tend to confirm the negative results obtained by treating tetrolic and with sodium amalgam.

Further action of bromine on tetrolic acid.

It was next attempted to add four atoms of bromine to tetrolic acid, producing tetrabromobutyric acid.

The first experiment consisted in dissolving the calculated amount of bromine in chloroform and running it gradually from a separating funnel into a chloroform solution of tetrolic acid standing in ice water, after half the bromine had been run in the colour no longer disappeared upon standing. It was therefore removed from the ice water and left at the ordinary temperature of the room for 5 days, but still remained colored. On removing the stopper a considerable amount of hydrobromic acid was given off and on evaporating the solution in a current of dried air, dibromocrotonic acid alone was obtained. It is clear therefore that at the ordinary temperature of the laboratory bromine has no action on dibromocrotonic acid. One and a half grams of dibromocrotonic acid were then dissolved in chloroform in a tube and the calculated amount of bromine required for the addition of 2 atoms of bromine was dissolved in chloroform and added to the solution. The tube was sealed up and heated to 100° for a week. On opening the tube (whose contents were still colored with free bromine) no pressure was observed, but a certain amount of hydrobromic acid was given off. The liquid was destilled off on a water bath, what remained was left to crystallise out at the ordinary temperature in the air and proved to be unaltered dibromocrotonic acid. On evaporating however the last portions of the mother liquor on a watch glass in vacuo a few crystals were obtained melting several degrees higher than dibromocrotonic

acid, but the melting pt. was not sharp and the amount of substance was too small to permit of its investigation.

Three grams of dibromocrotonic acid were then placed in a tube and the calculated amount of bromine required for the addition of 2 atoms was added dissolved in as small an amount of chloroform as possible. The tube was sealed up and heated to 100° for 3 weeks in a water bath.

On opening the tube (which was still colored with free bromine, a considerable quantity of gas was evolved and also a large amount of hydrobromic acid.

The liquid was evaporated in a current of dry air till a syrup remained which soon began to deposit small white crystals. The whole was placed on a watch glass and left for several hours in vacuo. The mass was then treated with cold chloroform in which liquid the crystals were almost insoluble. After repeated washing with chloroform to remove the syrup, the crystals were dissolved in boiling chloroform and separated out on cooling in beautiful small white feathery tufts showing a melting pt. of 131·5—132°. This melting pt. remained constant after recrystallisation.

A bromine determination of the substance gave the following figures

Substance taken	·1998
wt of Ag Br formed	·3497
wt of Br	= ·1488

% of bromine calculated for tetrabromobutyric	% of Br found	% of bromine calculated for tribromocrotonic acid
79·20	74·47	74·30

another bromine determination gave

wt of substance taken	·1886
wt of Ag Br formed	·3301

% of Br found	calculated for tribromocrotonic
74·44	74·30

It would seem then that the substance formed is tribromocrotonic acid and not tetrabromobutyric acid. In all probability bromine unites with dibromocrotonic acid to form the tetrabromo

compound, and this latter by the splitting off of hydrobromic acid yields the tribromocrotonic acid. The mother liquor after as much as possible of the pure tribromo compound had been obtained was evaporated in the air for several days and the residue neutralised with carbonate of sodium and agitated with ether to remove any neutral oil that might be present. It was then acidified with hydrochloric acid and again extracted with ether. The extract after pressing between filter paper and drying in vacuo was dissolved in hot water. The crystals which separated out on cooling were washed and recrystallised from hot water in white needles, which melted at 120° and consisted of unaltered dibromocrotonic acid. The disengagement of so large a quantity of gas on opening the tube, indicated a considerable amount of decomposition and this proved to be the case; not more than half a gram of pure tribromocrotonic acid was obtained and only a very small quantity of the original acid, from 3 grams of dibromocrotonic acid used. It is probable that carbon dioxide and bromallylene may have been among the products formed

this $CH_3\ CB_2\ CBr\ COOH$
$= COO + HBr + CH_3C \equiv CBr$

Further experiments on the tribromocrotonic acid were precluded from want of material. It is possible that by acting on the dibromo compound for a longer time at a lower temperature a better yield might be obtained.

Life.

I — M. C. Clutterbuck — was born in London in 1865 and removed to Bath in 1875, I studied privately till 1879, when I went to Somerset College and matriculated from that college at the London University in 1883. I then entered University College Bristol, where I studied Chemisty, Physics, Botany, Zoology and Geology.

In 1886 I passed the Intermediate examination for the BSc. degree of the University of London, and the following year, took the degree of Bachelor of Science. I continued to work for another year at University College Bristol and in 1888 matriculated at the Imperial University of Strassburg where I have since studied, principally chemistry, though hearing also lectures in Botany and Physic.

M. C. CLUTTERBUCK.

Strassburg, July 28th. 1891.